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**THE EFFECT OF RESIDUAL LIGNIN CARBOXYL AND OTHER  
ACID GROUPS ON OXYGEN BLEACHABILITY OF KRAFT PULP**

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on Oxygen Bleachability of Kraft Pulp**

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## THE EFFECT OF RESIDUAL LIGNIN CARBOXYL AND OTHER ACID GROUPS ON OXYGEN BLEACHABILITY OF KRAFT PULP

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### ABSTRACT

As part of a study to identify structural features of residual lignin that enhance its ease of removal during oxygen delignification, a series of experiments was done to assess the importance of the content of carboxylic and other acid groups. Kraft pulp was subjected to various types of pretreatments, each of which has been previously demonstrated to have a beneficial effect on oxygen stage selectivity. These consisted of nitrogen dioxide, chlorine, sodium sulfite, and ozone. Carboxyl groups were introduced by all treatments except sodium sulfite. The sulfite treatment introduced some strongly acidic groups, which may be assumed to be sulfonic acid groups. An attempt to correlate the selectivity of a subsequent oxygen stage with the sum of the contents of carboxylic and strongly acidic groups showed that no single correlation exists for all pretreatments, but selectivity generally increases within each as acid group content increases. It was concluded that acid groups contribute modestly to the ease of lignin removal during oxygen delignification and, therefore, to the selectivity of that process. There is, however, no dominating influence of such groups on lignin removal from pretreated pulps by oxygen and alkali.

### INTRODUCTION

Modern kraft mills increasingly employ oxygen delignification before chlorination to decrease requirements for chlorine and chlorine-containing bleaching chemicals. This trend has recently intensified, owing to a growing desire to reduce the formation of chlorinated organic byproducts in both the bleaching effluent and the bleached pulp.

Conventional application of oxygen predelignification leads to a reduction in unbleached lignin content and a corresponding reduction in chlorine demand of 40-50%. More extensive delignification is normally precluded by the limited selectivity of the oxygen stage, which results in losses of pulp viscosity and strength at high degrees of delignification. On the other hand, laboratory studies have demonstrated that certain chemical pretreatments of the unbleached pulp increase the selectivity of a subsequent oxygen stage. They include nitrogen oxides<sup>1,2</sup> chlorine<sup>3,4</sup>, chlorine dioxide<sup>5</sup>, ozone<sup>3,6</sup>, hydrogen peroxide<sup>5</sup>, and sodium sulfite<sup>7</sup>. Their use allows the upper limit on oxygen delignification to be substantially increased from its normal level of about 50%.

Application of any of these pretreatments, followed by oxygen delignification under a fixed set of conditions, has two major effects on the properties of the pulp emerging from the oxygen stage. These are a decrease in kappa number and an increase in viscosity. The kappa number decrease demonstrates the existence of an accelerating effect of the pretreatments on the delignification reactions. The viscosity increase may be due to a protective effect of the pretreatment agent or its reaction products on cellulose. On the other hand, it may simply be due to a reduction in average alkalinity due to more rapid consumption of alkali by sensitized residual lignin. We favor the latter interpretation, in view of an earlier observation that addition of NO<sub>2</sub>-treated lignin to cotton linters had no effect on the linters' viscosity after treatment under simulated oxygen delignification conditions<sup>8</sup>. This interpretation implies that to understand the mechanism of action of the pretreatments studies should be focused on their acceleration of delignification reactions.

The mechanism by which any pretreatment accelerates subsequent oxygen delignification may involve one or more of the following component mechanisms: a decrease in the molecular mass of the lignin; an increase in its hydrophilicity; an increase in its sensitivity to depolymerization and solubilization under the conditions of oxygen delignification; cleavage or sensitization of lignin-carbohydrate linkages; and blocking of lignin condensation reactions.

The actual mechanisms, for the most part, remain unknown. They have received most attention in the case of treatment with NO<sub>2</sub>. Andersson et al.<sup>9</sup>, for example, have demonstrated the occurrence of the following changes in kraft lignin during NO<sub>2</sub> treatment: demethylation, loss of phenolic hydroxyl groups, increase in titratable acid groups, and nitration. In a similar, more recent study, Larsson et al.<sup>10</sup> showed increases in acid groups and hydrophilic properties and the formation of ester groups. Ester formation was associated with an increase in the molecular mass of the lignin, which was, in turn, attributed to the hot acidic conditions of the pretreatment. Hot alkali treatment of the modified lignins resulted in a rapid reversion of molecular mass to its untreated level. This was attributed to cleavage of intermolecular ester linkages. In some samples, the alkali reduced the molecular size to levels below that of the original pulp, suggesting that ether linkages may have been rendered sensitive to alkali by the treatment. In others, however, the molecular size of the alkali-treated lignin remained higher than that of the untreated sample. These observations suggest that rendering the lignin hydrophilic may be important but that depolymerizing the lignin or rendering it sensitive to depolymerization may not be.

Lindeberg and Walding<sup>11</sup> speculated that nitration of nonphenolic units makes residual lignin more susceptible to depolymerization by facilitating alkaline hydrolysis of alkyl-aryl ether bonds. A more recent study by Ohi and McDonough<sup>12</sup>, however, shows that nonphenolic model compounds are not nitrated under conditions of the pretreatment, rendering the Lindeberg-Walding mechanism unlikely.

It is apparent from the above review that much remains to be done in gaining an understanding of selectivity-improving pretreatments for oxygen. In fact, this objective can be usefully generalized to include effects of all processes to which the pulp is subjected before it enters an oxygen delignification stage, including the pulping process. Stated in this way, the objective becomes that of identifying structural features of residual lignin that enhance the response of pulp-to-oxygen delignification.

The purpose of the study described here was to assess the importance of one such structural feature, the content of carboxylic acid groups in kraft residual lignin. The likelihood that carboxyl groups and the hydrophilicity they impart to lignin are important contributors to ease of lignin removal has been suggested by several studies. Samuelson and co-workers, in the studies already referred to<sup>9,10</sup>, have shown that NO<sub>2</sub>-treated pulps consume more alkali in titrations to pH 9 than untreated pulps. Gellerstedt and Lindfors<sup>13</sup> have emphasized the importance of carboxyl introduction during bleaching and have shown that the carboxyl content of dissolved and isolated residual lignins correlates with the relative efficiencies of bleaching stage types. None of these studies, however, has addressed the degree to which carboxyl group introduction can account for the efficacy of pretreatments for oxygen bleaching.

The general approach we adopted was to subject kraft pulp to various types of pretreatments, each of which has been previously demonstrated to have a beneficial effect on oxygen stage selectivity. These consisted of nitrogen dioxide, chlorine, sodium sulfite, and ozone. Each pretreating chemical was applied at several different charge levels under otherwise similar conditions. The pretreated pulps were then analyzed for carboxyl group content prior to being subjected to oxygen delignification.

The method chosen for determination of carboxyl groups was that of Katz et al.<sup>14</sup>. It consists essentially of conductometric titrations of pulp samples previously equilibrated with dilute acid and subsequently washed. Sodium chloride was added to suppress Donnan equilibrium effects<sup>15</sup>.

## RESULTS AND DISCUSSION

### Analysis of Pretreated Pulps

The results of conductometric titrations of the untreated pulp and samples of the same pulp after treatment with 2 and 8% NO<sub>2</sub> are shown in Figure 1. Before each titration was begun, 1.5 mL of 0.1 N HCl was added. The descending portion of each curve is due to neutralization of conductive hydrogen ions originating with the added acid and any strongly acidic functional groups in the pulp. The flat portion at the bottom corresponds to neutralization of the titrant's hydroxyl ions by carboxyl groups bound to the pulp, the majority of which may be assumed to reside within the lignin component. Since these are weakly acidic, they do not contribute appreciably to the conductivity of the pulp suspension, and their

conversion to the salt form results in no change in conductivity. When all the carboxyl hydrogen ions have been consumed, continued addition of titrant contributes excess conductive hydroxyl ions, accounting for the ascending portion. The carboxyl content may be estimated from the consumption of titrant during the period characterized by constant conductivity. This is determined by drawing straight lines through the descending, ascending, and flat portions of the curve and measuring the distance between intersections on the flat portion. Consumption of titrant up to the point of the first intersection should be exactly equivalent to the amount of HCl added before beginning the titration unless strongly acidic groups (such as sulfonic acid groups) are present in the pulp. The amount of such groups present can thus be estimated from the position of this intersection along the titrant volume axis.

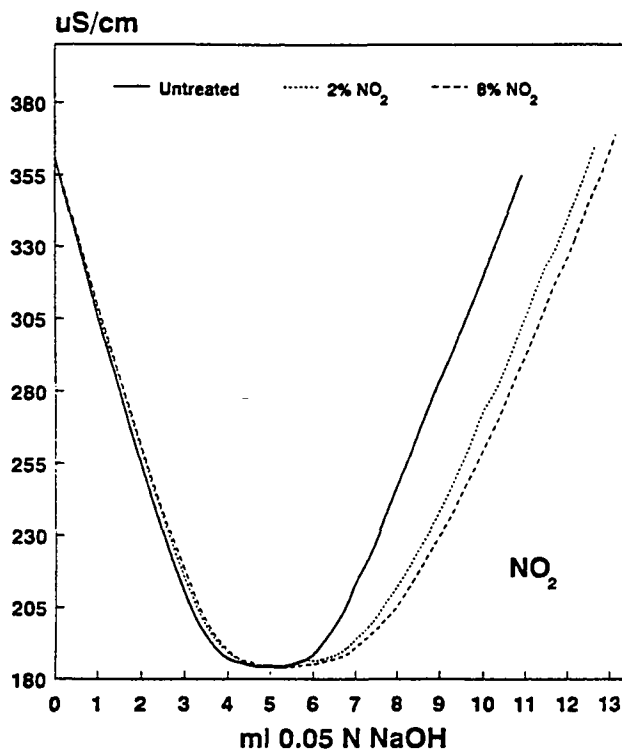


Figure 1: Conductometric titration curves for untreated pulp and pulps pretreated with 2 and 8%  $\text{NO}_2$ .

The results of Figure 1 confirm that carboxyl groups are introduced by  $\text{NO}_2$  treatment. The calculated carboxyl contents for the three samples shown were 100, 144, and 150 meq/kg, respectively. Small contents of strongly acidic groups also indicated are 11, 14, and 14 meq/kg, respectively. Determinations of the kappa numbers of these three pulps gave values of 39.5, 39.0, and 38.4, showing that little delignification had occurred during the pretreatment. Methoxyl contents were 353, 303, and 271 meq/kg. The reasonable agreement between the increases in carboxyl and reductions in methoxyl indicates that the carboxyl groups were introduced into the lignin component of the pulp. Figure 2 shows the corresponding titration curves for ozone-treated pulps. In this case, the width of the titration interval corresponding to carboxyl group neutralization decreased with increasing treatment level. This was due to delignification rather than to

removal of carboxyl groups from lignin and resulted from the large decreases in kappa number that accompanied ozone treatment. The kappa numbers of pulps treated with 0, 0.5, 1, and 2% ozone were 39.5, 34.5, 30.1, and 21.9, respectively. The carboxyl group contents of the lignin were 1.68, 1.83, 1.97, and 2.33 meq/g. The latter determinations were made by combining the conductometric titration and kappa number data and assuming that the lignin content (as % of o.d. pulp wt.) of a treated pulp is equal to 0.15 times its kappa number.

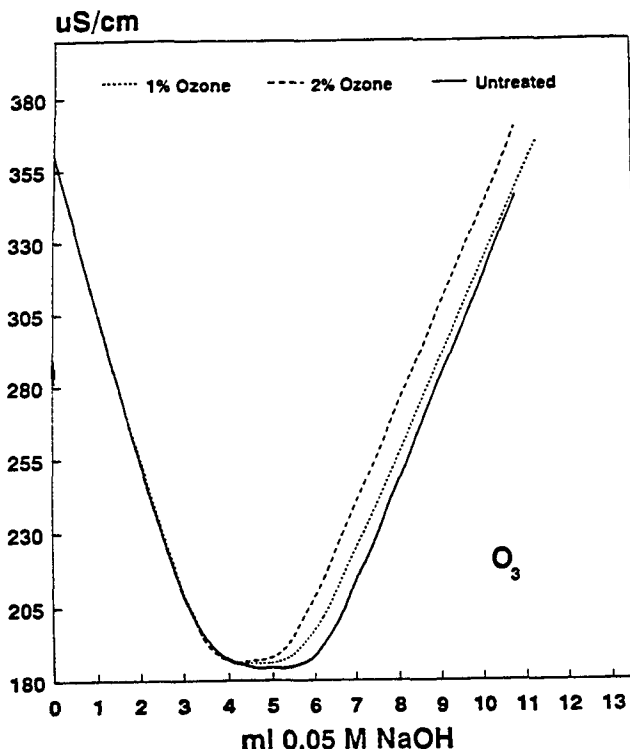


Figure 2: Conductometric titration curves for untreated pulp and pulps pretreated with 1 and 2%  $O_3$ .

The results of conductometric titrations of the remaining pretreated pulps are presented in Table 1, together with the results of determinations of their kappa numbers and methoxyl contents. Carboxyl groups were introduced by all treatments except that with sulfite. The sulfite treatment introduced some strongly acidic groups which may be assumed to be sulfonic acid groups. Total acid group content is shown in Figure 3 as a function of the type and amount of pretreating chemical applied. Nearly all of the acid groups introduced were carboxyl groups except in the case of the sulfite treatment.



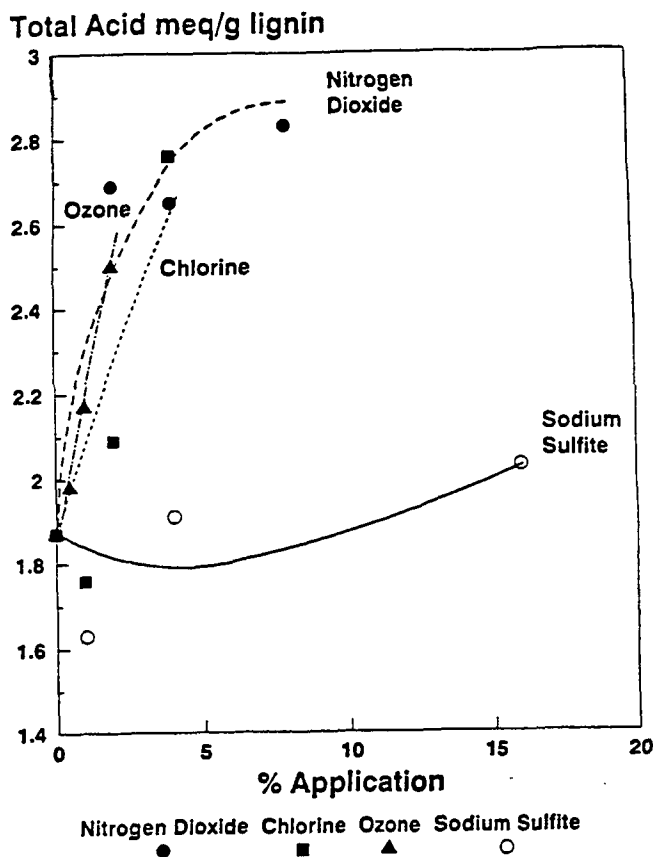


Figure 3: Total acid groups (sum of carboxyl and strongly acidic groups) as a function of chemical application for all pretreatments.

When calculated as a percentage of the lignin component (as estimated from kappa number), methoxyl contents generally decreased, as shown in Figure 4. This is to be expected when carboxyl groups are introduced into lignin by demethylation and ring oxidation with the formation of products such as substituted muconic acids. An apparent exception to the trend of decreasing lignin methoxyl content was the pulp treated with 2% ozone. The highly oxidized lignin in this pulp may have reduced permanganate demand in the kappa number test, leading to underestimation of the lignin content and overestimation of the methoxyl content of the lignin. In addition, ozone is capable of cleaving the aromatic ring of lignin model compounds without disrupting the linkage between the ring and the methoxyl group.

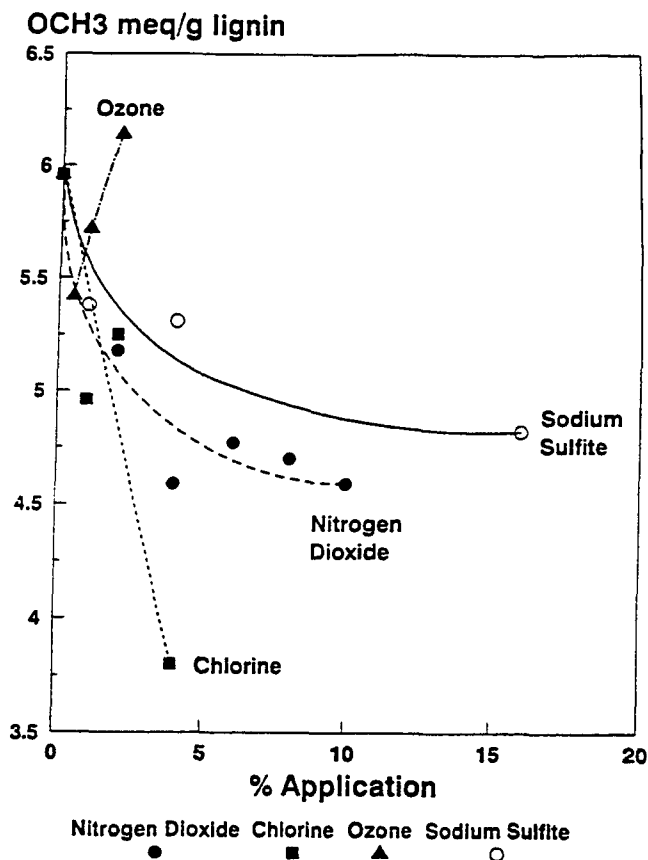


Figure 4: Methoxyl group content as a function of chemical application for all pretreatments.

### Oxygen Bleaching

To be effective, a pretreatment must possess two characteristics. The first is that it must be selective in itself; it must be able to extensively modify the residual lignin in a kraft pulp without simultaneously depolymerizing cellulose. The second is that it must confer selectivity upon an ensuing oxygen stage. The first characteristic can be measured by determination of viscosity before and after the pretreatment. The second is reflected by the relative changes in viscosity and kappa number that occur during the oxygen stage, relative to their values after the pretreatment. It may be quantitatively expressed as the inverse of the slope of the viscosity-kappa number relationship, averaged over the duration of the oxygen stage.

The emphasis in the present study was on the latter of these two characteristics and whether it depends on the introduction of carboxyl groups. Accordingly, the main objective of our oxygen bleaching experiments was to establish the degree of selectivity conferred by each pretreatment.

Subsamples of each pretreated pulp were oxygen bleached at 25% consistency and approximately 100 deg. C with 1, 2, and 4% NaOH addition, based on the dry weight of the pulp sample. To avoid pretreatments of large amounts of pulp, microscale bleaching reactors and microanalytical procedures were used to

evaluate the resulting bleached pulps. Since the bleaching procedure was newly developed and of unproven precision, all bleaching runs, with one exception, were done in duplicate. In addition, untreated controls were included with each batch of samples.

Figure 5 shows the kappa number and viscosity data for all of the untreated control samples except for two outlying points which were discarded. The line drawn through these points is included in Figures 6-9 for reference.

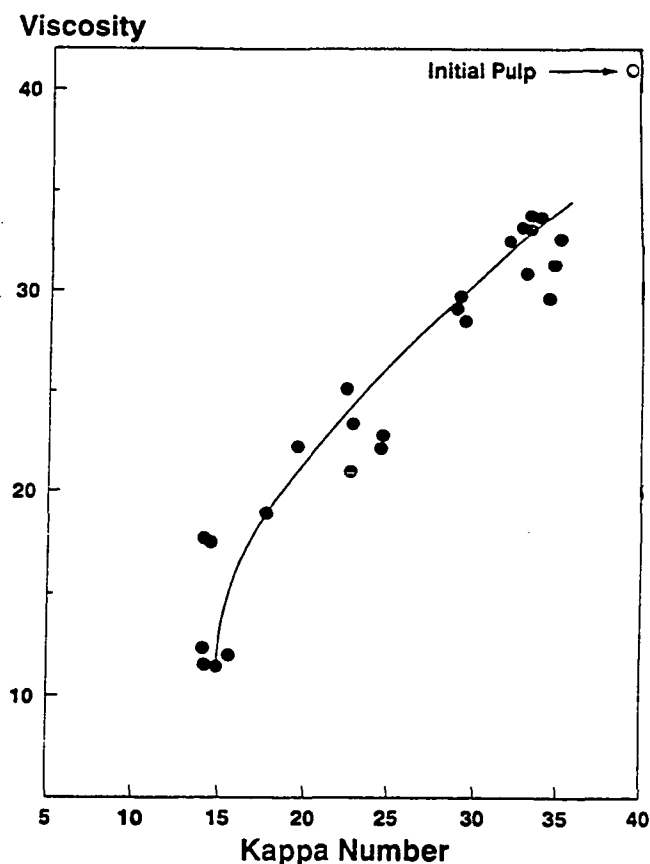


Figure 5: Viscosity as a function of kappa number after oxygen bleaching for untreated pulps.

The results of oxygen bleaching of nitrogen dioxide pretreated pulps are shown in Figure 6. As expected, treatment with 2%  $\text{NO}_2$  brought about a significant improvement in selectivity, while larger additions had relatively small additional effects.

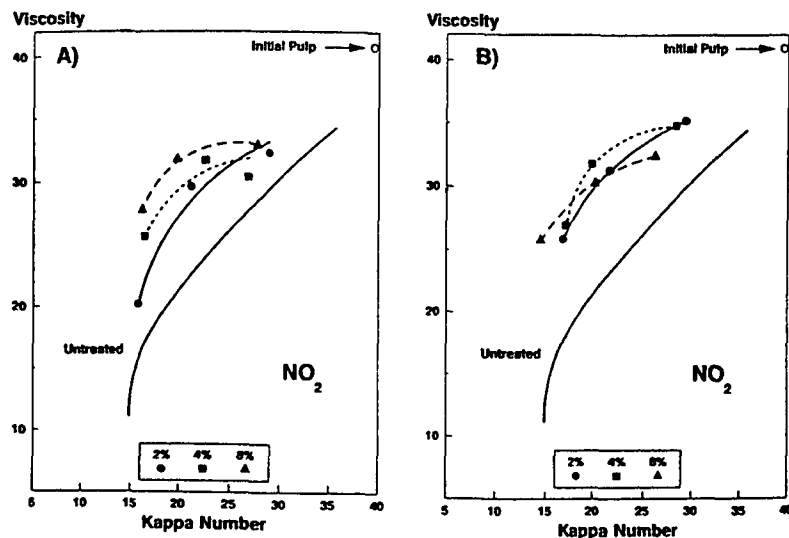


Figure 6: Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with nitrogen dioxide. Data for two complete replicates, (A) and (B), are shown.

Figure 7 contains the corresponding results of chlorine pretreatments. For this pretreatment, the selectivity improvement was strongly dependent on post-oxygen kappa number. As the chlorine charge was increased, the maximum selectivity improvement became larger and occurred at lower kappa numbers. During the first of the two replicate runs shown in Figure 7, some difficulty was encountered with reactor temperature control, with the result that this run was conducted at a significantly lower temperature than the second one. The temperature decrease resulted in improved selectivity for the pretreated pulps but not for the controls. A final observation of interest is that the highest chlorine application resulted in an apparent viscosity increase during oxygen bleaching. This may be due to removal of low-molecular-weight material or may reflect improved stability of the oxygen-bleached pulps toward depolymerization by the solvent used in the viscosity determination.

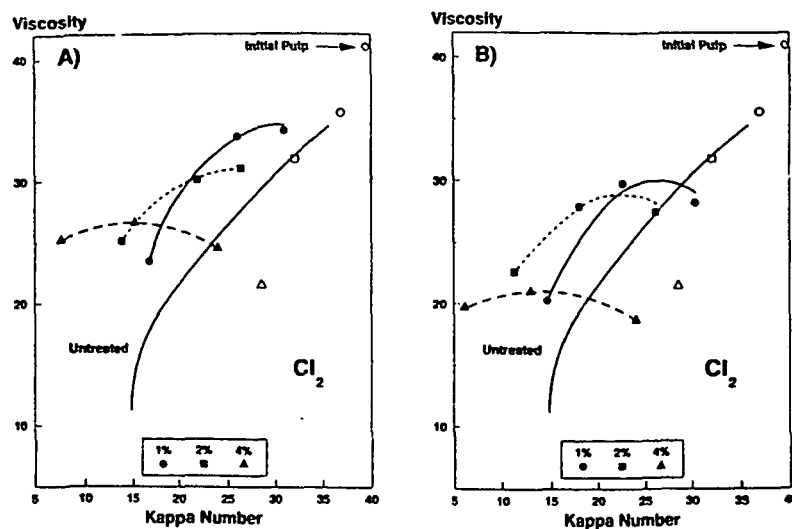


Figure 7: Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with chlorine. Data for two complete replicates, (A) and (B), are shown.

Treatment with ozone before oxygen bleaching gave the results shown in Figure 8. The pretreatment itself was less selective than oxygen, but it did confer relatively high selectivity on the oxygen stage, as evidenced by the low slope of the curves shown.

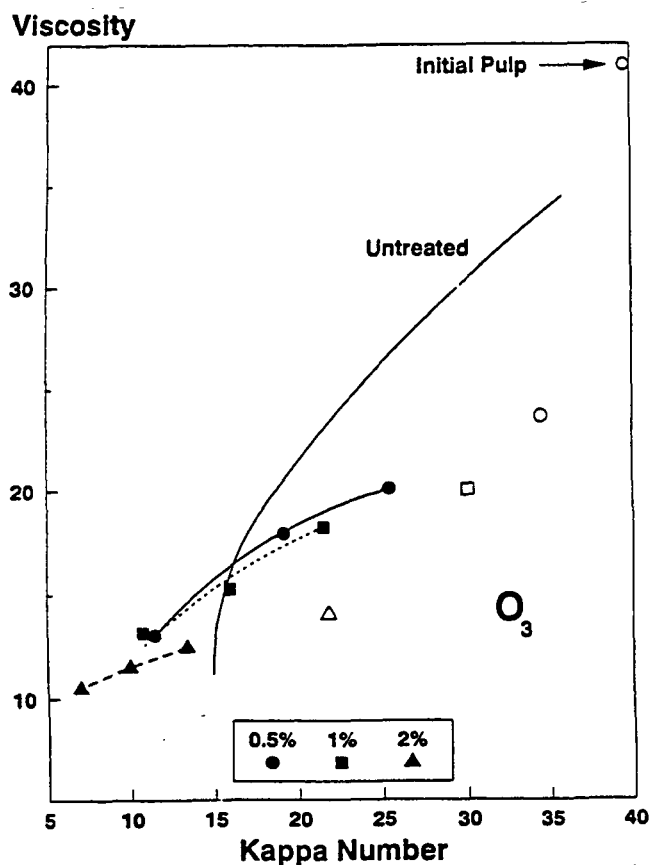


Figure 8: Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with ozone.

Treatment with sodium sulfite, as shown in Figure 9, also reduced the slope of the viscosity-kappa number relationship but not by a sufficient amount to offset a viscosity loss incurred during the pretreatment itself.

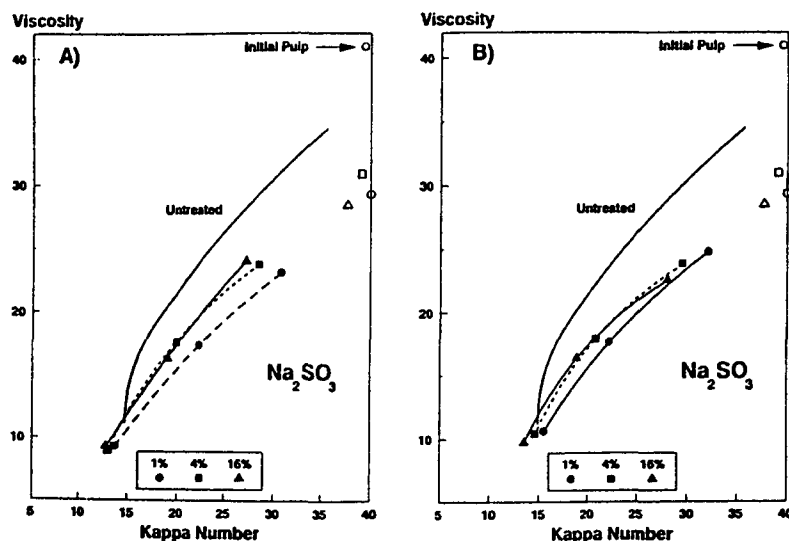


Figure 9: Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with sodium sulfite. Data for two complete replicates, (A) and (B), are shown.

### Acid Groups and Selectivity

For each of the curves shown in Figures 6-9, selectivity during the oxygen stage was measured as the decrease in kappa number divided by the decrease in viscosity in reducing the lignin content of the pretreated pulp by 50%. Averaging the results for both replicates gave the oxygen stage selectivity values shown in Table 1. Figure 10 shows the results of an attempt to correlate these with the sum of the contents of carboxylic and strongly acidic groups. It is apparent that no single correlation exists for all pretreatments, but selectivity generally increases within each as acid group content increases. This suggests that although a strong cause-effect relationship does not exist, the hydrophilicity conferred on lignin by acidic groups contributes to the ease of lignin removal during oxygen bleaching.

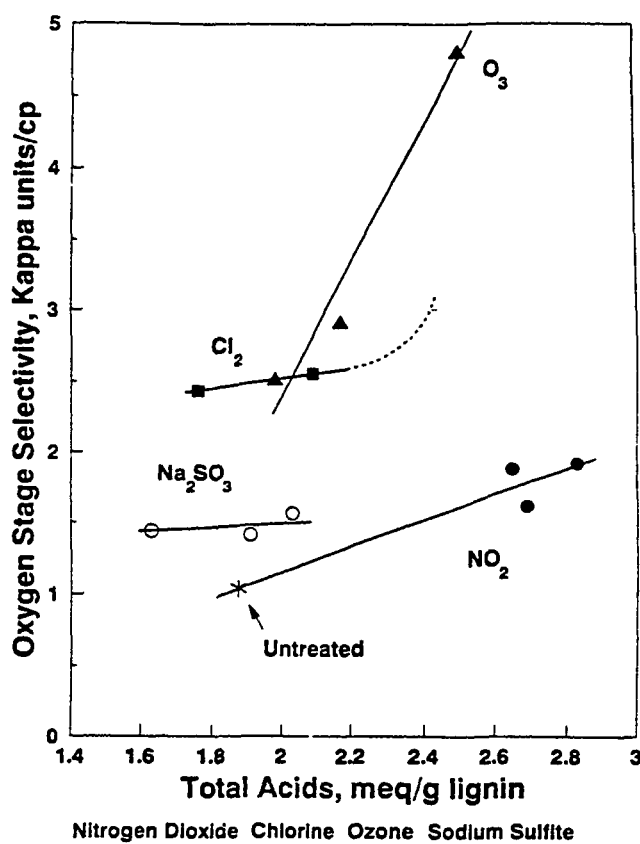


Figure 10: Oxygen stage selectivity vs. total acid group content for all pretreatments.

To reiterate one of our introductory remarks, selectivity during the oxygen stage is only one of two necessary characteristics of a good pretreatment-oxygen sequence. It combines with the selectivity of the pretreatment itself to determine the selectivity of the sequence. One measure of the latter quantity is the viscosity after the oxygen stage at a given overall degree of delignification, as shown in Table 1. The superiority of nitrogen dioxide and chlorine over the other two pretreatments, not apparent from Figure 10, can be traced to the selectivity of the pretreatment itself.

## CONCLUSIONS

Acid groups in unbleached kraft pulps, believed to reside in the residual lignin component, contribute modestly to the ease of lignin removal during oxygen delignification and, therefore, to the selectivity of that process. There is, however, no single relationship between acid group content and selectivity for different pretreatments and, therefore, no dominating influence of such groups on lignin removal from pretreated pulps by oxygen and alkali.

## EXPERIMENTAL

### Material

Never-dried industrial southern pine kraft pulp with a kappa number of 39.5 and a CED viscosity of 40.6 cP was used in all experiments. The pulp was stored at 4 °C and 33% consistency. After the initial experiments on nitrogen dioxide pretreatment, it was determined that shives in the pulp caused poor repeatability in the kappa number and viscosity tests after oxygen bleaching. The pulp was therefore screened and stored at 4 °C and 34% consistency for use in the remaining experiments. Kappa number and viscosity tests on the screened pulp were within experimental error of the results obtained for the unscreened pulp.

The kraft pulp was pretreated with the chemicals and conditions given in Table 2.

### Pulp Testing

Unbleached and pretreated pulps were analyzed for carboxyl, methoxyl, kappa number, and viscosity. Oxygen-bleached pulps were analyzed for kappa number and viscosity. With few exceptions, all tests were performed on duplicate samples.

### Nitrogen Dioxide Treatment

Nitrogen dioxide treatment followed the technique reported by Andersson and Samuelson<sup>16</sup> except that the amount of pulp was adjusted to give an exact percentage of NO<sub>2</sub> application. After fluffing, 43 to 45 o.d. grams of pulp was placed in a 2-liter round bottom flask, and the air in the flask was evacuated with a vacuum pump. Nitrogen dioxide was then slowly admitted into the rotating flask from a small pipet in which the nitrogen dioxide had been accurately weighed. After five minutes, zero-grade oxygen was swept through the pipet thereby transferring the nitrogen dioxide completely into the reaction flask. After the pressure in the flask had reached 760 torr, rotation of the flask was continued for an additional 10 minutes at room temperature. The gas in the flask was then slowly withdrawn through a standardized NaOH solution to trap any unreacted nitrogen oxides. Titration of the NaOH solution showed no evidence of reactive components in the gas phase within the flask. Cold distilled water was then added to the pulp to 6% consistency and the pulp was filtered. Titration of the filtrate with NaOH showed a linear increase in acidity with an increasing level of NO<sub>2</sub> application. Absorbance readings of this filtrate also showed a linear increase in absorbance at 280 nm versus the level of NO<sub>2</sub> application. The pulp was washed two additional times at about 5% consistency, filtered, and stored at 4 °C and 25% consistency.



## Chlorination

The chlorinations were carried out in a stirred glass resin kettle at 3% consistency for 30 minutes at 25 °C. The pulp was filtered and washed with several portions of distilled water. The pulp was then air dried to between 45% and 81% consistency and fluffed in preparation for oxygen bleaching.

## Ozone Treatment

The ozone treatments were performed at atmospheric pressure in a rotating glass reactor of the same type used in the nitrogen dioxide pretreatment. The ozone was produced from zero-grade oxygen with a Welsbach model T816 ozone generator. Prior to treatment, the pulp was washed with 0.08 M acetic acid and filtered. The pulp was then air dried to 30% consistency and fluffed before ozone treatment. After ozone treatment, the pulp was washed at 3% consistency, filtered, and stored at 4 °C and 22% consistency.

## Sodium Sulfite Treatment

Sodium sulfite was mixed with 20 o.d. grams of pulp in a Hobart mixer at 20% consistency. Treatments of pulp with sodium sulfite were performed in 500 mL stainless steel vessels heated in an oil bath with a temperature ramp from ambient to 140 °C in 30 minutes. Because of the small size of the reaction vessels, the treatments were performed in duplicate for each application level and the pulps then combined. The combined pulps were fluffed and air dried in preparation for oxygen bleaching.

## Oxygen Delignification

To prepare samples for alkaline oxygen bleaching, the pulp samples were partially air dried and fluffed. To ensure a homogeneous sample for both nitrogen dioxide- and ozone-treated pulps, the pulps were gently disintegrated in a blender prior to air drying. The time between pretreatments varied from four days in the case of chlorinated pulps to several weeks for nitrogen dioxide-treated pulps. Bleach trials were performed in a stainless steel pressure vessel of 2.2-liter capacity which could accommodate 12 samples of pulp of 3 o.d. grams each. The 12 samples were composed of the three application levels of each pretreatment and three untreated control samples with NaOH charge levels of 1%, 2%, and 4%. All samples were treated with 0.1%  $\text{MgSO}_4$  as  $\text{Mg}^{2+}$ . To apply caustic/ $\text{MgSO}_4$  solution at a consistency of 26%, 3 o.d. grams pulp samples were tared in 100 mL plastic beakers, and the impregnation solution was dispersed in the pulp by compressing the pulp several times so that the solution was released and reabsorbed by the sample. The samples were then taken in random order, fluffed by hand, and placed in perforated PVC cups which were then stacked in the pressure vessel. After charging with 70 psig oxygen at room temperature, the vessel was heated in an oil bath for 70 minutes with the average temperature over the last 30 minutes ranging from 87-104 °C. After bleaching, samples were washed with 200 mL of distilled water at which time a pH reading was taken. The

sample was filtered, disintegrated in 1 liter of distilled water, and filtered again on a coarse fritted funnel. The pulp pad was allowed to air dry for later testing of kappa number and CED viscosity.

### Conductometric Titrations

Initially, conductometric titrations were performed using the procedure reported by Pu and Sarkanen.<sup>15</sup> It was found that this procedure could be modified in two principal ways and still produce reproducible results. The tests could be scaled down so that only 1.5 o.d. grams of pulp was used in each determination of acid group content. In addition, the rate of addition of titrant could be increased substantially without changing the result by a significant amount. After being stirred in 300 mL of 0.1 M HCl for about one hour, the pulp was filtered on a small fritted funnel and washed exhaustively with distilled water. The pulp was then dispersed in 250 mL of 0.001 M NaCl and 1.5 mL of 0.1 M HCl added to the solution. The conductivity of this solution generally was about 385 uS/cm except for Na<sub>2</sub>SO<sub>3</sub>-treated pulps which had a conductivity of over 400 uS/cm. Additional 0.001 M NaCl was then added dropwise to the solution thereby reducing the conductivity to a common point for all titrations performed. The solution was titrated with freshly prepared 0.05 M NaOH solution. The alkali was added in units of 0.25 mL from a 10 mL buret while bubbling nitrogen through the solution to eliminate effects from CO<sub>2</sub> absorption. Since volume changes during titrations were only about 4%, volume corrections were not necessary. A Markson Electromark Analyzer was used for conductivity measurements and NIST traceable standardized acid and base solutions were obtained from commercial sources.

A disadvantage of the conductometric method is that it requires acid washing of the pulp which could lead to a reduction in carboxylic acid content by lactone formation<sup>14</sup>. Slow addition of titrant would seem to be necessary in order that lactones formed during acid washing are hydrolyzed during the titration. It was found that speeding up the rate of the titration to less than one hour gave results only a few percent lower than titrations performed over several hours. In addition, extending the length of time in which the pulp was soaked in acid did not affect the results.

Conductometric titration curves of pulp suspensions are characterized by three linear regions. Initially, excess acid is neutralized by titrant, and the conductivity descends in a linear fashion. The first transition at a pH of about 4 occurs when the pulp begins to be ionized. While the pulp is in an intermediate state of ionization, the conductivity remains constant as the pulp consumes titrant. The length of this linear region is a measure of the carboxylate content of the pulp. The end of the titration is then characterized by a linear region where the conductivity increases due to excess titrant. To calculate values from the titration curves, lines were drawn through each of the aforementioned linear regions thereby obtaining two end points where the lines intersect. The value for strong acid content in the pulp was obtained by subtracting the equivalents of strong acid added before the titration from the equivalents corresponding to the first

end point. The value for carboxylate content was obtained by subtracting the equivalents corresponding to the first end point from the number of equivalents corresponding to the second end point. The average repeatability was 5%.

### **Methoxyl Determinations**

Methoxyl analysis was done by Chem-Lig International Industries, Inc. (320 Ross Avenue, Schofield, WI 54476, USA) by reacting the test samples with HI and determining the resultant methyl iodide liberated by the sample. The average repeatability was 9%.

### **Kappa Number and Viscosity**

Kappa number tests were at 1/10 the scale of the TAPPI test method T236 with an average repeatability of about 1.7%. CED viscosity tests were by TAPPI test method T230 with repeatability generally less than 4%.

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**Table 1: Experimental Pretreatment Data**

Pretreatment Chemical Type	Charge, %o.d.p.	Kappa No. After Pretreatment	Functional Groups, meq/g lignin <sup>a</sup>				Viscosity After Pretreatment, cp.	Oxygen Stage Selectivity <sup>e</sup> ΔK/ΔV	Pretreatment Selectivity ΔK/ΔV	Post-Oxygen Viscosity at 50% Delignification, cp. <sup>f</sup>
			OCH <sub>3</sub>	COOH	Strong Acids	Total Acids				
None		39.5	5.96	1.68	0.19	1.87	40.6	1.04		21.8
NO <sub>2</sub>	2	39.0	5.18	2.45	0.24	2.69	40.6 <sup>b</sup>	1.61 <sup>b</sup>	n.a. <sup>d</sup>	28.6
	4	38.4	4.59	2.40	0.24	2.65	40.6 <sup>b</sup>	1.88 <sup>b</sup>	n.a. <sup>d</sup>	30.6
	8	38.4	4.70	2.59	0.24	2.83	40.6 <sup>b</sup>	1.92 <sup>b</sup>	n.a. <sup>d</sup>	30.8
Cl <sub>2</sub>	1	36.8	4.96	1.59	0.17	1.76	35.6	2.43	0.53	27.2
	2	32.2	5.25	1.92	0.18	2.09	31.8	2.55	0.84	28.2
	4	28.6	3.80	2.47	0.29	2.76	21.6	n.a. <sup>c</sup>	0.57	22.4
Na <sub>2</sub> SO <sub>3</sub>	1	40.0	5.38	1.37	0.26	1.63	29.4	1.44	0.0	15.8
	4	39.1	5.31	1.54	0.38	1.91	31.0	1.41	0.0	17.5
	16	37.7	4.82	1.47	0.57	2.03	28.5	1.56	0.15	17.5
O <sub>3</sub>	0.5	34.5	5.42	1.83	0.15	1.98	23.7	2.50	0.29	18.2
	1	30.1	5.72	1.97	0.20	2.17	20.1	2.90	0.46	17.2
	2	21.9	6.14	2.33	0.17	2.50	14.1	4.80	0.66	13.0

**Notes:**

- After estimating lignin content from: % lignin (o.d. pulp basis) =  $0.15 \times \text{Kappa no.}$
- Viscosity not measured after NO<sub>2</sub> pretreatment; it was assumed that viscosity was unaffected by the pretreatment.
- Viscosity of 4% Cl<sub>2</sub>-treated pulp increased during oxygen stage.
- Not measured. May be assumed to be high.
- For 50% removal of the lignin in the pretreated pulp.
- After 50% removal of the lignin in the untreated pulp.

**Table 2: Pretreatment conditions**

Pretreatment level	Consistency %	Temperature °C	Reaction time minutes	Application % on o.d. pulp
NO <sub>2</sub>	33	25	15	2%, 4%, 8%
Cl <sub>2</sub>	3	25	30	1%, 2%, 4%
O <sub>3</sub>	30	25	10	0.5%, 1%, 2%
Na <sub>2</sub> SO <sub>3</sub>	20	140	30	1%, 4%, 16% <sup>a</sup>

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<sup>a</sup>as SO<sub>2</sub>